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CRITICAL REVIEW ON VAPOR-LIQUID
EQUILIBRIUM OF HYDROGEN ISOTOPE
MIXTURE FOR FUSION APPLICATION

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CRITICAL REVIEW ON VAPOR-LIQUID EQUILIBRIUM OF HYDROGEN ISOTOPE
MIXTURE FOR FUSION APPLICATION

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Since the relative volatilities for the D_2 -DT- T_2 system are close to unity (the values for D_2 -DT or DT- T_2 are in the range from 1.1 to 1.3), even minor errors in the relative volatilities lead to a considerable error in the number of total stages required for a cryogenic distillation column to meet the prescribed output specifications. Thus, the extent of nonideality (or equivalently, the Raoult's Law deviation) is a major concern in simulation studies for the columns. Sherwood and Souers proposed an estimation procedure for the deviation of hydrogen isotope mixtures, but the deviation experimentally observed for mixtures including tritium is significantly higher than that predicted by the procedure. They thought that this discrepancy was ascribed to the too large deviation apparently observed stemming from a temperature sensor problem caused by tritium x-ray effects. The authors doubt that the sensor problem is the only factor affecting the too large deviation observed, and give some discussion on expected radio-chemical effects by tritium on the deviation.

KEYWORDS : Relative Volatility, Hydrogen Isotopes, Cryogenic
Distillation, Raoult's Law, Ideal Mixture, Tritium,
Nonideality, Radiation

核融合研究における水素同位体混合物の気液平衡
に関する批評的レビュー

日本原子力研究所那珂研究所核融合研究部

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D_2-DT-T_2 系の相対揮発度は1に近い(D_2-DT , $DT-T_2$ のそれは1.1から1.3の範囲にある)ため、相対揮発度の小さな誤差も、深冷蒸留塔で規定された出力条件を満たすのに必要な段数の計算値の大きな誤差に結びつく。このように、水素同位体溶液の非理想性(あるいはラウールの法則からのずれの大小)は、塔のシミュレーション研究においてきわめて重要である。Sherwood と Souersは、水素同位体溶液のラウールの法則からのずれの推定法を提出しているが、トリチウムを含む溶液に対しては、ずれの推定値は実測値よりもかなり小さい。彼らは、トリチウムのX線によって温度センサーが影響を受け、その理由のみから、ずれが実際よりも過大に観測されてしまうのだと結論している。著者らは、この結論に疑問を投げかけ、トリチウムの放射化学的效果によっても、ずれがより大きくなるのではないかという新しい考え方を提示すると共に、若干の考察を行った。

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1. INTRODUCTION

It is well recognized that cryogenic distillation is one of the most reliable methods for achievement of hydrogen isotope separation in the fusion fuel cycle. To analyze static and dynamic behaviors of the distillation columns, an estimation procedure which allows us to describe the vapor-liquid equilibrium of hydrogen isotope mixtures is absolutely needed. The mixtures to be considered comprise the six molecular species : H_2 , HD, HT, D_2 , DT and T_2 , and are therefore multicomponent systems. Additionally, since there are a number of situations where hydrogen isotope separation is needed and the input and output specifications vary greatly from situation to situation, the estimation procedure is required to be capable of dealing with a wide range of composition. Unlike in the case of water isotopes, the hydrogen isotope mixture does not quite obey the ideal form of Raoult's Law owing to the relatively large isotope effects. Thus, the extent of non-ideality of the mixtures is a major concern in the prediction of the vapor-liquid equilibrium.

The cryogenic falling liquid film helium separator^{1,2} was proposed by one of the authors (M. Kinoshita) as an attractive process for removing helium from hydrogen isotopes. In the simulation of this process, the solubility of helium in the hydrogen isotope mixture (or equivalently, the volatility of helium in the He- H_2 -HD-HT- D_2 -DT- T_2 system) is a key physicochemical parameter and should therefore be studied.

In the present paper, the authors make a brief review of the previously reported works on the vapor-liquid equilibrium of hydrogen isotope mixtures from a viewpoint of fusion application, thus raising some problems to be solved in future studies : And the review is extended to mixtures of helium and hydrogen isotopes.

2. BRIEF REVIEW OF PREVIOUSLY REPORTED EXPERIMENTAL WORKS

Outlines of the previously reported experimental works on the vapor-liquid equilibrium of hydrogen isotope mixtures are given in TABLE I. Newman and Jackson³ studied the n-H₂-HD and n-H₂-n-D₂ systems, and reported the positive deviation from Raoult's Law. Bigeleisen and Kerr⁴ measured the vapor-liquid equilibrium ratios of HT and DT for dilute solutions of HT in e-H₂ and of DT in e-D₂, respectively. They noted that the equilibrium ratio of HT was appreciably smaller than that of e-D₂ for the dilute solution of e-D₂ in e-H₂. Bereznyak et al.⁵ made extensive measurements of the vapor-liquid equilibrium for the e-H₂-e-D₂ system. A significant result found by them was that the relative volatility for e-H₂-e-D₂ was a decreasing function of the mole fraction of e-H₂ in the liquid phase : For instance, the relative volatility observed at 20 K was larger than the ideal value in the range where the liquid H₂-mole fraction was lower than 0.45, and smaller in the range where it was higher than 0.45. Souers⁶ examined the data by Newman & Jackson and by Bereznyak et al., and found no appreciable ortho-para effects.

Sherman et al.⁷ measured the relative volatilities for the n-D₂-DT-n-T₂ system, and reported that the values were generally 5 to 6 % below the values predicted for the ideal mixtures. This result indicates that the extent of nonideality of the D₂-DT-T₂ system does not differ appreciably from that of the H₂-HD-D₂ system. Souers et al.⁸ studied Raoult's Law deviations for

the n-H₂-HT-n-T₂ and n-D₂-DT-n-T₂ systems. The observed deviations are shown in Fig. 1 where I_m is given by

$$I_m = 100(P - P^{\text{ideal}})/P^{\text{ideal}}. \quad (1)$$

The Raoult's Law pressure is given by

$$P^{\text{ideal}} = \sum_i x_i p_i^* . \quad (2)$$

Both the H-T and H₂-D₂ lines show I_m decreasing with temperature. Souers et al. emphasized that the sensor used for measurement of temperature underwent the tritium x-ray effects, and this perplexing sensor problem caused apparent deviations much larger than the actual deviations. They stated that the D-T data in Fig. 1 was clouded by the sensor problem. Thus, they thought that the extent of nonideality of the D₂-DT-T₂ system reported by Sherman et al. and shown in Fig. 1 was considerably higher than the actual extent. Since the isotope effects of the D₂-DT-T₂ system are expected to be smaller than those of the H₂-HD-D₂ system, their thought appears to be reasonable. However, the authors doubt that the unexpectedly large deviation observed is ascribed merely to the sensor problem, and this subject will be discussed later from a viewpoint of radiochemistry.

3. ESTIMATION PROCEDURE PROPOSED BY SHERWOOD AND SOUERS FOR RAOULT'S LAW DEVIATION

To our best knowledge, the procedure proposed by Sherwood and Souers⁹ for estimating the Raoult's Law deviation is the only one that has ever been published. The final result of their procedure can be expressed by the following :

$$K_i = \xi_i K_i^{\text{ideal}} , \quad (3)$$

$$K_i^{\text{ideal}} = p_i^*/P , \quad (4)$$

$$\ln \xi_i = \bar{G}_i^E / (RT) + B_i (p_i^* - P) / (RT) , \quad (5)$$

$$\bar{G}_i^E = \sum_j x_j A_{ij} - G^E \quad (6)$$

and

$$G^E = (1/2) \sum_i \sum_j x_i x_j A_{ij} . \quad (7)$$

Thus, the deviation coefficient is calculated as a function of temperature and liquid composition. The first and second terms in the right side of Eq.(5) represent the liquid-phase and vapor-phase nonidealities, respectively. The liquid-phase interaction coefficient, A_{ij} , is calculated from temperature by using the equation developed by Sherwood and Souers. For example, the value

of A_{ij} for each isotopic pair at 22.5 K is calculated as given in TABLE II. They state in their report that the ortho-para effects are negligibly small in the vapor-liquid equilibrium. It should be noted here that the Sherwood-Souers procedure does not account for the radiation effects by tritium.

The contributions of the vapor-phase and liquid-phase non-idealities to the total nonideality are illustrated for the H_2-D_2 system in Fig. 2. As observed from the figure, it is the liquid mixing term that dominates the overall behavior of the Raoult's Law deviation.

4. EXAMINATION OF SHERWOOD-SOUERS PROCEDURE

Figure 3 shows the Raoult's Law deviations for some representative mixtures calculated by using the Sherwood-Souers estimation procedure. Figure 3 should be compared with Fig. 2. Since cryogenic distillation is operated at a temperature in the range from 20 to 25 K, the deviations in this range can be considered more significant. The H₂-D₂ line in Fig. 3 is in relatively close agreement with the line in Fig. 2. Although the qualitative aspects of the H-T lines in Fig. 3 are almost identical with those in Fig. 2, the deviations experimentally observed are significantly higher than the predicted deviations. As for the D-T lines, P in Eq.(1) is close to P^{ideal} ; so the I_m -values experimentally determined undergo the sensor problem to a serious extent. Consequently, the D-T lines in Fig. 3 do not agree with those in Fig. 2 even in qualitative aspects.

TABLE III describes a comparison between the experimentally observed values of the relative volatilities and the values calculated by using the Sherwood-Souers procedure. The values estimated for the ideal mixtures are also given in the table. The comparison can be made only for the data reported by Berezhnyak et al., Sherman et al. and Bigeleisen & Kerr because the other workers did not report the relative volatilities. Although only two examples are given for the H₂-D₂ system in the table, it is verified that the relative volatilities estimated by the Sherwood-Souers procedure are in relatively close agree-

ment with those reported by Bereznyak et al. in a wide range of temperature and composition. However, the procedure tends to underestimate the extent of nonideality of the D_2 -DT- T_2 system. Souers et al. recognized this and thought that it was ascribed to the experimental errors caused by the above-mentioned sensor problem. Although the sensor problem is doubtlessly a major factor affecting the observed nonideality, the authors suspect that some radiation effect could be also a significant factor. In fact, even in cases of very low tritium concentration (see the data by Bigeleisen & Kerr in TABLE III) and where no sensor problem would be raised, the relative volatility calculated for D_2 -DT is considerably larger than the experimentally observed value.

As for cryogenic distillation columns, the number of total stages needed to satisfy the prescribed output specifications is roughly proportional to $(\ln\alpha)^{-1}$, where α denotes the relative volatility. If α is close to unity, then

$$\ln\alpha \sim \alpha - 1 . \quad (8)$$

Hence, even a small decrease in α results in a significant increase in the number of total stages needed. In other words, even a minor error in α leads to a considerable error in the number of the total stages calculated. The α -values for D_2 -DT or DT- T_2 are in the range from 1.1 to 1.3, so the extent of nonideality has significant effects on design of a D-T separating column.

Although no comparison is made for the H_2 -HT- T_2 system in TABLE III, it is expected that the relative volatilities estimated by using the Sherwood-Souers procedure are larger than the experimentally observed values for this system as well. The relative volatilities for the H_2 -HT- T_2 system are significantly larger than unity, so the errors in their values are less serious than in the case of the D_2 -DT- T_2 system. However, to understand actual behaviors of hydrogen isotope mixtures, the mixtures including tritium must further be studied from both theoretical and experimental standpoints.

In the mixtures including tritium, the β -ray of tritium causes ionizations of hydrogen isotopes. As a consequence, the cluster ions such as $(T_{2n+1})^+$ ($n = 1, 2, 3$) are formed by ion-molecule reactions of the ions (H^+ , D^+ and T^+) with the molecular species. In fact, H_3^+ , H_5^+ and H_7^+ ions have been observed in mass spectrometric investigations.^{10,11} The formation of these cluster ions in the mixtures can possibly affect the extent of nonideality.

5. SOLUBILITY OF HELIUM IN HYDROGEN ISOTOPE MIXTURE

The solubility of helium in hydrogen isotope mixtures was measured by Hiza¹² for the $^3\text{He-H}_2$, $^4\text{He-H}_2$, $^3\text{He-D}_2$ and $^4\text{He-D}_2$ systems, but the data reported suffers serious chemical analysis errors.¹³ Sherman¹³ measured the helium solubility for the $^4\text{He-H}_2$, $^3\text{He-D}_2$, $^4\text{He-D}_2$, $^3\text{He-T}_2$ and $^4\text{He-T}_2$ systems, but he has never published the data. Thus, there is essentially no reliable data of the helium solubility except the data for the $^4\text{He-H}_2$ system in a very high pressure range.¹⁴ The operating pressure of the cryogenic falling liquid film helium separator is about 1 atm¹ (or in the range from 1 to 2 atm), so the solubility should be measured in this practical pressure range. All information we presently know is the following : The solubility of helium can approximately be determined by Henry's Law ; the solubility is an increasing function of temperature ; helium is less soluble in D_2 than in H_2 ; and ^4He is a little more soluble than ^3He in H_2 or D_2 . Hence, experimental studies for the helium solubility must extensively be promoted. The final goal is to predict the vapor-liquid equilibrium of the $^4\text{He}(\text{or } ^3\text{He})\text{-H}_2\text{-HD-HT-D}_2\text{-DT-T}_2$ system in a wide range of temperature and composition.

Like in the case of hydrogen isotope mixtures, there is an interesting radiochemical effect to be noted here. It is expected that ^3He is less soluble in T_2 (or $\text{D}_2\text{-DT-T}_2$) than in D_2 . However, there remains the question of whether additional

^3He can be bounded in liquid tritium following some sort of radiation-induced reaction.¹⁵ In fact, the presence of $^3\text{HeT}^+$ and $^3\text{HeH}^+$ ions produced by tritium decay of T_2 and HT molecules has been verified in radiochemical studies by Wexler¹⁶ and Izawa et al.¹⁷ Thus, not all the ^3He formed by tritium decay outgases from the mixture with the result that the solubility of ^3He could apparently be increased.

6. CONCLUSION

Although the Sherwood-Souers procedure describes the vapor-liquid equilibrium of the H_2 -HD- D_2 system adequately well, the extent of nonideality predicted by the procedure for mixtures including tritium is significantly smaller than the experimentally observed extent. The authors doubt that this discrepancy is ascribed merely to the sensor problem pointed out by Souers et al., and have presented a concept that ionizations of hydrogen isotopes caused by the β -ray of tritium can possibly affect the vapor-liquid equilibrium. The authors are planning to initiate experimental studies to examine their concept.

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The authors wish to express their sincere thanks to Dr. M. Tanaka, Mr. Y. Naruse and Dr. H. Yoshida for the encouragement and guidance.

6. CONCLUSION

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The authors wish to express their sincere thanks to Dr. M. Tanaka, Mr. Y. Naruse and Dr. H. Yoshida for the encouragement and guidance.

NOMENCLATURE

A	= liquid-phase interaction coefficient
B	= pure-component second virial coefficient
G^E	= excess molar Gibbs free energy for a mixture
\bar{G}^E	= partial molar excess Gibbs free energy
K	= vapor-liquid equilibrium ratio
P	= total pressure
p^*	= vapor pressure for a pure component
R	= molar gas constant
T	= absolute temperature
x	= liquid mole fraction
α	= relative volatility
ξ	= deviation coefficient

(Superscript)

ideal : ideal mixture obeying Raoult's Law

(Subscript)

i : component index

j : component index

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TABLE I Outlines of Previously Published Experimental Works
on Vapor-Liquid Equilibrium of Hydrogen Isotope
Mixtures

System (Mixture)	Composition	Workers
n-H ₂ -HD, n-H ₂ -n-D ₂	H ₂ : 10 - 90 %	Newman & Jackson
e-H ₂ -HT, e-D ₂ -DT	HT/H ₂ = 10 ⁻⁸ , DT/D ₂ = 10 ⁻⁸	Bigeleisen & Kerr
e-H ₂ -e-D ₂	H ₂ : 5 - 95 %	Bereznyak et al.
n-D ₂ -DT-n-T ₂	T/D = 0.01 - 0.06	Sherman et al.
n-H ₂ -HT-n-T ₂ , n-D ₂ -DT-n-T ₂	T : 35 - 75 %	Souers et al.

Note : Souers⁶ examined the data by Newman & Jackson and by Bereznyak et al. and found no appreciable ortho-para effects on the vapor-liquid equilibrium. Hence, the authors do not specify 'normal (n-)' or 'equilibrium (e-)' in the succeeding discussion.

TABLE II Liquid-Phase Interaction Coefficients Calculated
by Using Sherwood-Souers Procedure (at 22.5 K)

H ₂ - HD	9.77*
H ₂ - D ₂	25.0
HD - D ₂	6.83
H ₂ - HT	16.7
H ₂ - T ₂	39.6
HT - T ₂	9.78
D ₂ - DT	1.55
D ₂ - T ₂	4.29
DT - T ₂	1.28

*) The unit is 'J/mol'.

TABLE III Comparison between Experimentally Observed Relative Volatilities and those Predicted by Using Sherwood-Souers Procedure

Temperature (K)	Liquid mole fractions	α -value observed	α -value predicted	α -value for ideal mixture
19.0	H ₂ : 0.700E-1	H ₂ -D ₂ :	H ₂ -D ₂ :	H ₂ -D ₂ :
	D ₂ : 0.300E-1	2.93	2.97	3.38
22.0	H ₂ : 0.900E-1	H ₂ -D ₂ :	H ₂ -D ₂ :	H ₂ -D ₂ :
	D ₂ : 0.100E-1	2.15	2.15	2.61
23.0	D ₂ : 0.937	D ₂ -DT :	D ₂ -DT :	D ₂ -DT :
	DT : 0.624E-1	1.185	1.225	1.249
	T ₂ : 0.111E-2	D ₂ -T ₂ :	D ₂ -T ₂ :	D ₂ -T ₂ :
		1.455	1.490	1.557
25.0	D ₂ : 0.948	D ₂ -DT :	D ₂ -DT :	D ₂ -DT :
	DT : 0.509E-1	1.159	1.182	1.208
	T ₂ : 0.599E-3	D ₂ -T ₂ :	D ₂ -T ₂ :	D ₂ -T ₂ :
		1.382	1.391	1.459
24.163	D ₂ : 1.000	D ₂ -DT :	D ₂ -DT :	D ₂ -DT :
	DT : 0.100E-7	1.163	1.198	1.225
20.250	H ₂ : 1.000	H ₂ -HT :	H ₂ -HT :	H ₂ -HT :
	HT : 0.100E-7	2.009	2.012	2.304

Note : The H₂-D₂ data was reported by Berezhnyak et al., the D₂-DT-T₂ data was cited from the paper by Sherman et al., and the D₂-DT and H₂-HT data were reported by Bigeleisen & Kerr.

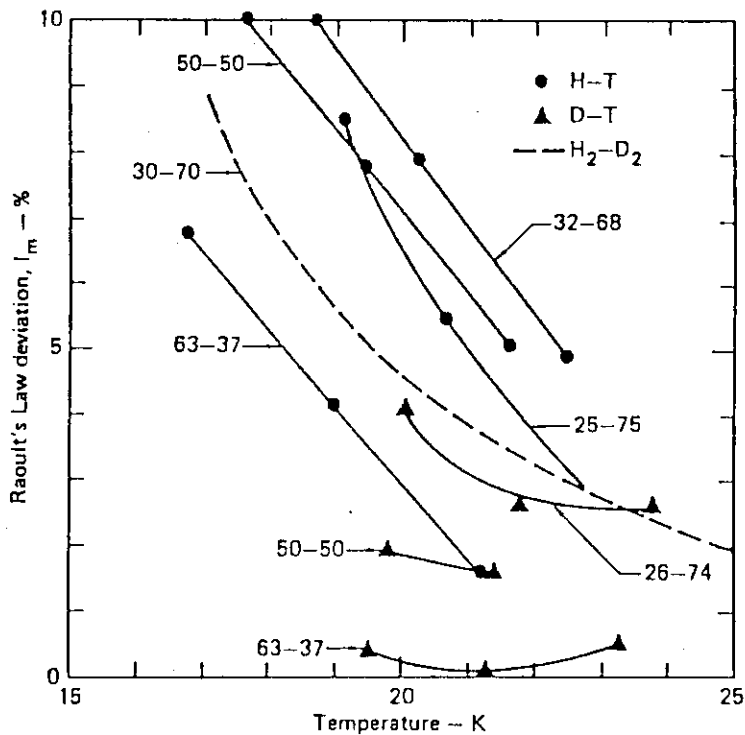


Fig. 1 Raoult's Law deviations experimentally observed by Souers et al.

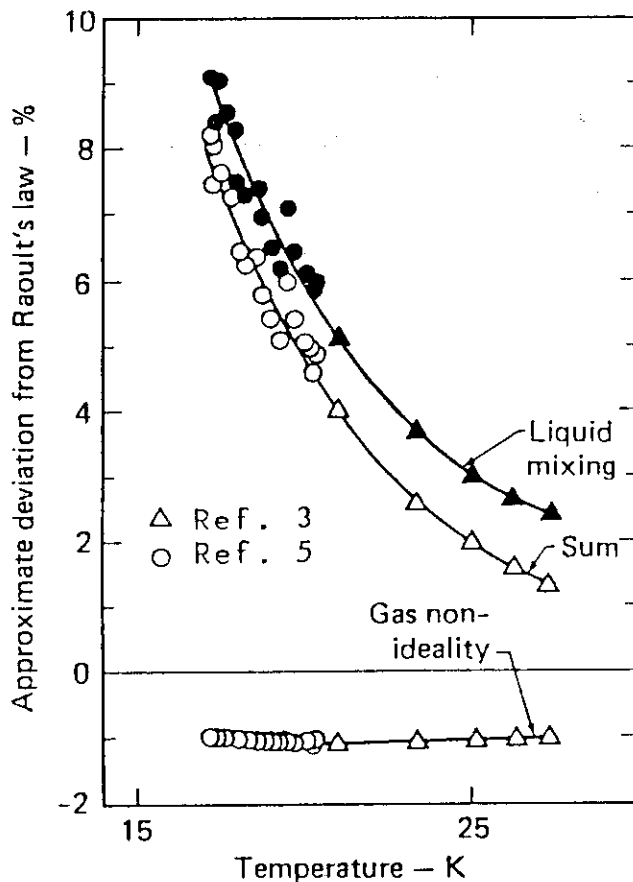


Fig. 2 Contributions of vapor-phase and liquid-phase nonidealities to the total nonideality for the H_2-D_2 system.

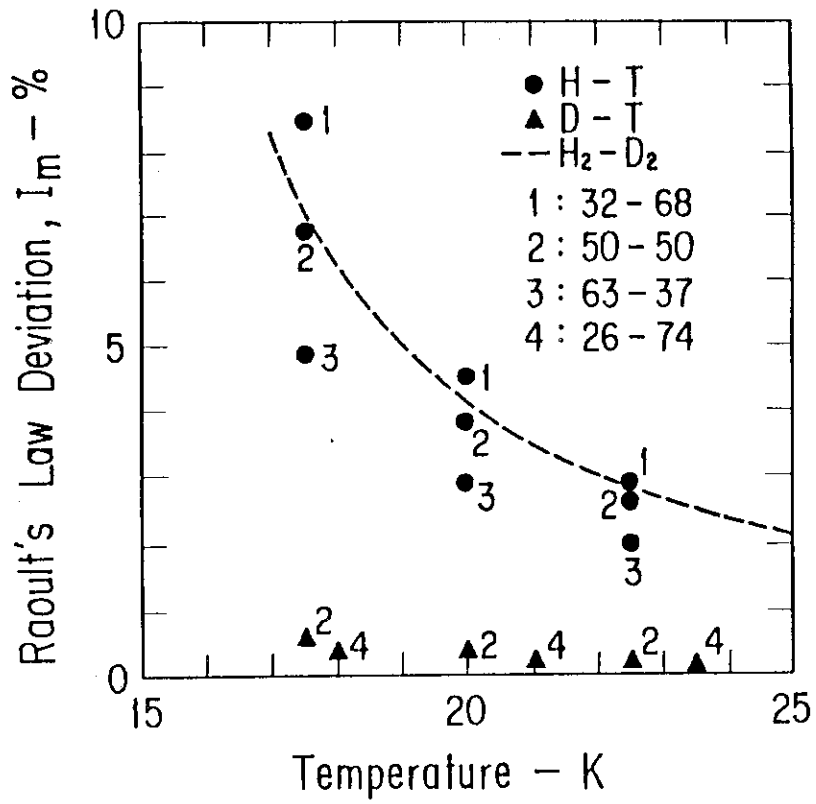


Fig. 3 Raoult's Law deviations estimated by using the Sherwood-Souers procedure.